

Towards a Theory of Transport in Disordered Organic Polymers: Poly(*p*-Phenylene Vinylene) (PPV)

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The emergence of organic electronic devices, including light-emitting diodes and field-effect transistors, fabricated from conjugated polymers such as poly(*p*-phenylene vinylene) (PPV), has stimulated research into the electrical and optical properties of these semiconducting polymers. The nature of the charge-trapping states that stem from the conformational disorder in these systems has not been clearly identified from a structural perspective. A complete description of these electronic materials is challenging because they are highly disordered and interactions between molecules are very important in determining their properties. Despite extensive experimental and theoretical research, there is still a limited understanding of these strongly interacting disordered materials.

Our approach uses a combination of classical molecular dynamics (MD) and density functional theory (DFT) to investigate the role of intra-molecular conformational disorder and inter-molecular electronic interactions on the electronic structure of disordered clusters of PPV. Classical molecular dynamics is used to determine probable molecular geometries for the interacting disordered oligomers (Fig. 1). For an ensemble of such configurations, the electronic structure and associated energy levels are determined with first-principles density functional theory (Fig. 2). Intra-molecular and inter-molecular effects are disentangled by contrasting results for densely packed oligomer clusters with those for ensembles of isolated oligomers with the same intra-molecular geometries (Fig. 3). We find that in PPV, electron trap states are induced primarily by intra-molecular configuration disorder, while the hole trap states are generated primarily from inter-molecular electronic interactions. The molecular orbitals responsible for the deep trap states can be examined (Fig. 4), and associated with specific conformational properties.

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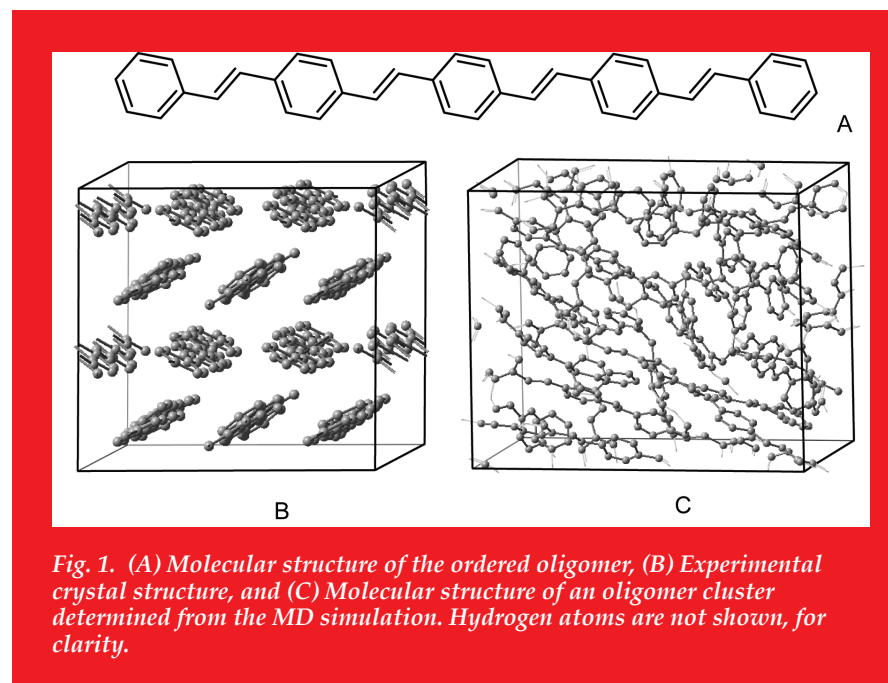


Fig. 1. (A) Molecular structure of the ordered oligomer, (B) Experimental crystal structure, and (C) Molecular structure of an oligomer cluster determined from the MD simulation. Hydrogen atoms are not shown, for clarity.

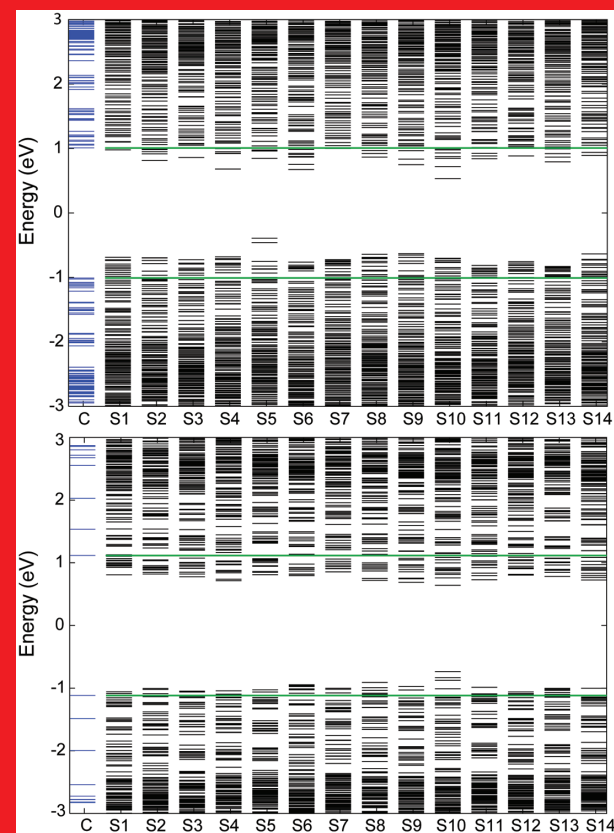


Fig. 2. Energy level diagrams from the DFT calculations. The upper panel shows results for the ideal crystal (left) and 14 disordered oligomer clusters whose geometry was determined from the MD calculations; the lower panel shows results for an isolated ordered oligomer (left) and an ensemble of 12 isolated oligomers with the same molecular geometries as in the corresponding column of the upper panel.

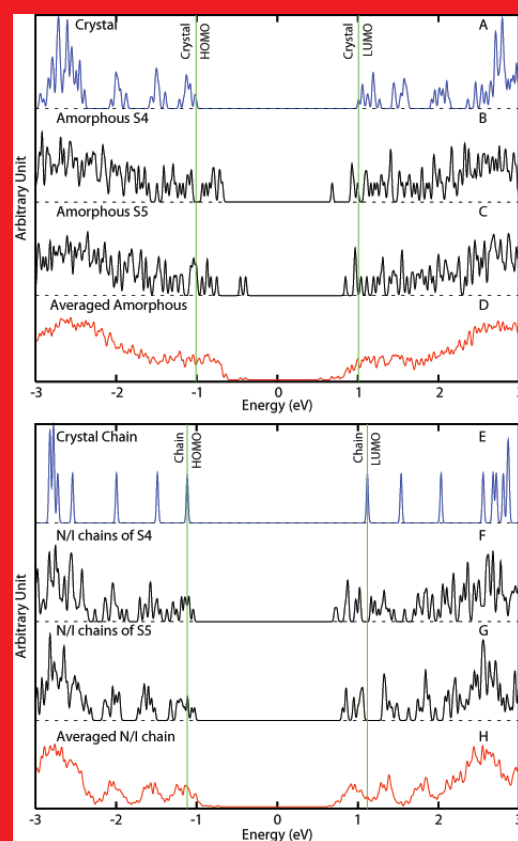


Fig. 3. Calculated density of states for: (A) the ideal crystal, (B) disordered cluster S4, (C) disordered cluster S5, (D) the ensemble average of clusters S1-S14, (E) the isolated oligomer in the ideal crystal, (F) the 12 isolated oligomers in cluster S4, (G) the 12 isolated oligomers in cluster S5, and (H) the ensemble average of isolated oligomers in clusters S1-S14. Note that green lines denote different energy gaps in top panels A-D versus bottom panels E-H.

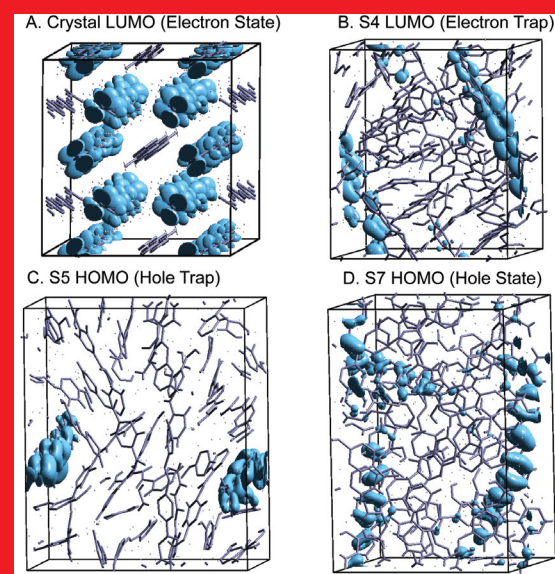


Fig. 4. Calculated electron densities for selected states: (A) the crystal lowest unoccupied molecular orbital (LUMO) state, (B) the LUMO level for cluster S4, (C) the highest occupied molecular orbital (HOMO) level for cluster S5, and (D) the HOMO level for cluster S7.